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TECHNICAL REPORT ARCSL-TR-80001

RATE OF WETTING OF STANDARD ARMY FABRICS BY BIS(2-ETHYLHEXYL) HYDROGEN PHOSPHITE

by

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Research Division

April 1980

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US ARMY ARMAMENT RESEARCH AND DEVELOPMENT COMMAND
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Wetting, rate of

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The rate at which a droplet of liquid bis(2-ethylhexyl) hydrogen phosphite wets standard Army fabrics has been measured. The ratio of the area wetted at time T to the area wetted at the time the droplet first contacts the fabric is proportional to T raised to a power >0. By comparison with data collected in an earlier study, it is shown that the rate at which vapor from the droplet is transported from the fabric to a second underlying layer is proportional to the area wetted by the liquid.

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PREFACE

The work described in this report was authorized under Project 1L162706A553, Technical Area 3-4. This work was started in June 1978 and completed in March 1979. The experimental data are recorded in notebook 9659.

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RATE OF WETTING OF STANDARD ARMY FABRICS BY BIS(2-ETHYLHEXYL) HYDROGEN PHOSPHITE

I. INTRODUCTION.

Among the threats faced by soldiers in a chemical warfare (CW) environment is the possible employment by an enemy of liquid agents, either in neat form or thickened with polymers. The droplet of these liquids that will challenge the soldier might be 5 mm in diameter or even larger. These droplets will impact on the soldier's clothing. The objective of an ongoing research program has been to quantify the transport of liquid agent, disseminated as large droplets, from its impact on the outermost fabric layer to inner surfaces.

In a prior report, a study of the rate at which liquid droplets of bis(2-ethylhexyl) hydrogen phosphite ('bis'), statically placed on the surface of selected military fabrics, are transported to a second underlying layer was presented.* That study showed that the process involved transfer to the second layer in the vapor, rather than the liquid, phase.

A linear regression analysis applied to the data generated in that study showed that the mass of vapor transported to a second underlying layer was proportional to the logarithm of the elapsed time. The regression analysis did not identify a unique functional relationship between the quantity of mass penetrating, P, and the logarithm of the elapsed time. Rather, two possible functional relationships could describe the transport process; namely, the penetration, P. is proportional to LOG(T) or the logarithm of the penetration, LOG(P), is proportional to LOG(T). Consequently, the empirical equation found in that study can be written as

$$f(P) = KLOG(T) + C \qquad (1)$$

where K and C are empirical constants and the notation f(P) indicates some function of P, either P itself or LOG(P).

It was observed during the conduct of those experiments that the fabrics on which the liquid spread the most, i.e. wetted the most area, had the greatest quantities of vapor transported to the second layer. The rate at which vapor is transported to the second layer, if the available surface area and temperature are kept constant, should be linear as a function of time. The observation that the quantity transported to the second layer appears to depend on wetted area coupled with the unexpected logarithmic nature of the time dependence suggested that the area available for vaporization might be the controlling parameter in this transport process. In order to establish that vaporization was dependent on area, a study of the rate of wetting, or spreading rate, was undertaken. The objective of this study was to show that the area wetted was a function of LOG(T).

II. PROCEDURE.

The three fabrics used in this study were the same as those employed in the study referred to above. These are the thin cotton sateen material, 6.5 oz/sq yd, the 50% cotton-50% wool undergarment, and the thick cotton sateen, 8.5 oz/sq yd. The fabrics used were either new or had been washed as described in the earlier report. The liquid bis was used either as a neat liquid or thickened with PIBM** to an apparent viscosity of 1300 centistokes, measured at low

*Klein, J. M. Material Transport Through Fabrics from Statically Placed Droplets. In Press.
**Polyisobutylmethacrylate.

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shear rate on a Brookfield viscometer.* To increase the visibility of droplets when placed on the fabric surfaces, the liquids were dyed blue, using a small quantity of methylene blue. The droplets were dispersed using glass droppers to produce droplets of 3.3 and 4.4 mm for the neat liquid and approximately 4 mm for the thickened bis. The droplet size was determined from the equivalent spherical diameter for a droplet of known weight.

The experiment consisted of setting out swatches of fabric on a white piece of paper. Using weights placed at the edges, the fabric was held flat, but not stretched or under tension. A piece of graph paper, having major grid squares of 1-inch length and width, was placed adjacent to the fabrics. A 35-mm single-lens reflex camera, fitted with an f/3.5 35-mm wide-angle lens and an electronic flash unit, was mounted on a tripod directly over the fabrics. A Graymar laboratory timer was placed in the camera field of view beside the fabrics.** The camera was also fitted with a long cable release to permit taking pictures at the same time the droplet was placed on the fabric. The clock was started and a droplet was placed on the first piece of fabric. A photograph was taken immediately with the placement of each droplet. This procedure was repeated sequentially until each piece of fabric had one droplet on it. Photographs were then taken at convenient time intervals until the test was completed. The film was Kodak high-speed Ektachrome.

To measure the wetted area covered, the film was made into transparencies that were projected using a standard slide projector on to a sheet of white Xerox paper. The magnification achieved was approximately 1.5 times the actual size. The image of each droplet was traced on the paper. The image of the 1-inch calibration square was also traced. The time shown on the clock was noted on each transparency. Each sheet of paper was then cut apart and the tracings of the droplet imaged were cut out and weighed on an analytical balance. The image of the 1-inch square was also cut out and weighed. Using the weight of the 1-inch square as a standard, the areas of the droplets were calculated by dividing the droplet image weight by the inch standard weight.

III. RESULTS AND DISCUSSION.

The data collected using the procedures described are summarized in table 1. In the form presented, the data give total areas covered at the time the photograph was taken. These data provide a useful measure of the spread of the bis from the starting point of the droplet of known size. However, as presented here, the data are not amenable to interpretation as to the significance of the spreading of the liquid.

Accordingly, the data were recomputed. The ratio of the area covered at time T to the area at the time the droplet was first placed on the fabric was determined and plotted on various types of graph paper. It was determined, in this fashion, that a log-log plot gave the best straight lines. These results are shown in figures 1 to 3 for the 3.3-mm and 4.4-mm neat bis droplets and for the 1300-cs PIBM-thickened bis, respectively. By presenting the data in this form, the effect of scale is minimized and the functional relationship is clearly seen.

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*Model LV, Brookfield Engineering Laboratories, Inc., Stoughton, Massachusetts.

**Type 202, Dimco-Gray Company, Dayton, Ohio.

Table 1. Area Wetted by Bis on Fabrics

Time	Area wetted by 3.3-mm drop						Time	Area wetted by 4.4-mm drop						Time	Area wetted by thickened bis (4-mm diameter)					
	Fabric							Fabric							Fabric					
	A	B	C	D	E	F		A	B	C	D	E	F		A	B	C	D	E	F
sec	sq in						sec	sq in						sec	sq in					
37	0.28		0.05				3	0.30						4	0.06					
53	0.43		0.08				35	0.73	0.22					21	0.10	0.11				
74	0.44	0.28	0.08	0.07	0.32		63	0.71	0.56	0.10				39	0.14	0.15	0.09			
91	0.59	0.52	0.10	0.15			90	0.79	0.58	0.14	0.09			57	0.15	0.17	0.11	0.07		
200	0.63	0.51	0.07	0.17	0.16	0.24	111	0.68	0.65	0.13	0.17	0.09		74	0.17	0.24	0.14	0.11	0.09	
400	0.65	0.54	0.10	0.24	0.35	0.21	126	1.16	1.01	0.18	0.25	0.25	0.14	90	0.18	0.23	0.16	0.10	0.11	0.13
1000	1.12	0.77	0.10	0.29	0.36	0.41	200	1.08	1.00	0.21	0.32	0.29	0.40	200	0.22	0.34	0.17	0.17	0.25	0.28
4000	1.02	0.78	0.11	0.36	0.25	0.32	400	1.42	1.04	0.23	0.37	0.29	0.48	1000	0.41	0.41	0.25	0.27	0.42	0.40
6000	1.07	1.14	0.11	0.47	0.79	0.46	1000	1.47	1.13	0.21	0.45	0.51	0.51	4000	0.67	0.53	0.32	0.30	0.52	0.60
12000	0.86	1.24	0.13	0.51	0.38	0.49	3000	1.96	1.50	0.25	0.55	0.79	0.48	10000	0.89	0.72	0.33	0.38	0.78	0.65
							5000	1.76	1.46	0.29	0.68	0.85	0.51							

NOTE: Fabric designations:

A = New thin cotton fatigue.
B = Washed thin cotton fatigue.
C = New 50% cotton-50% wool undergarment.
D = Washed 50% cotton-50% wool undergarment.
E = New thick cotton fatigue.
F = Washed thick cotton fatigue.

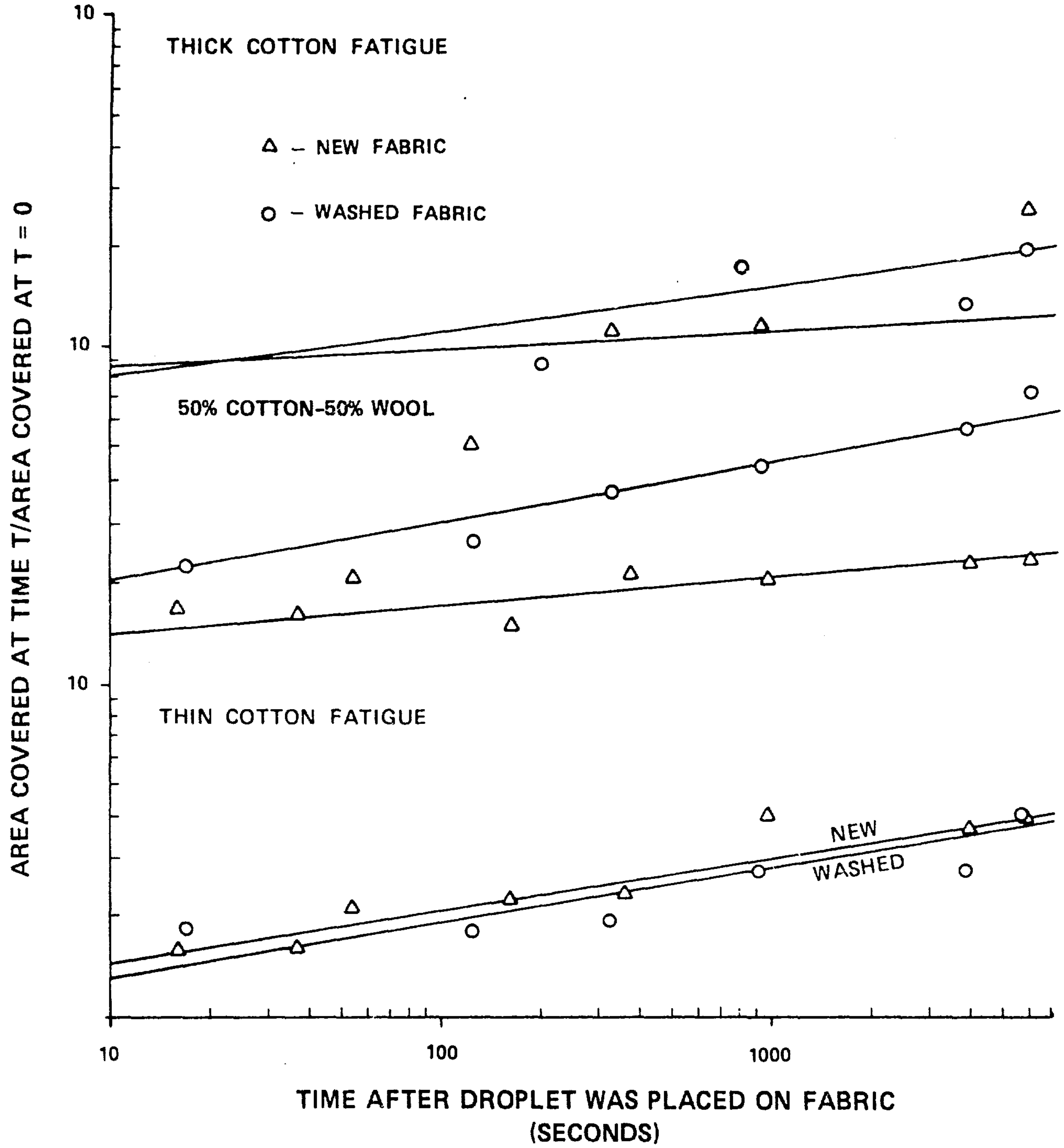

Figure 1. Spread of Neat Bis (3.3-mm Drops) on Fabrics

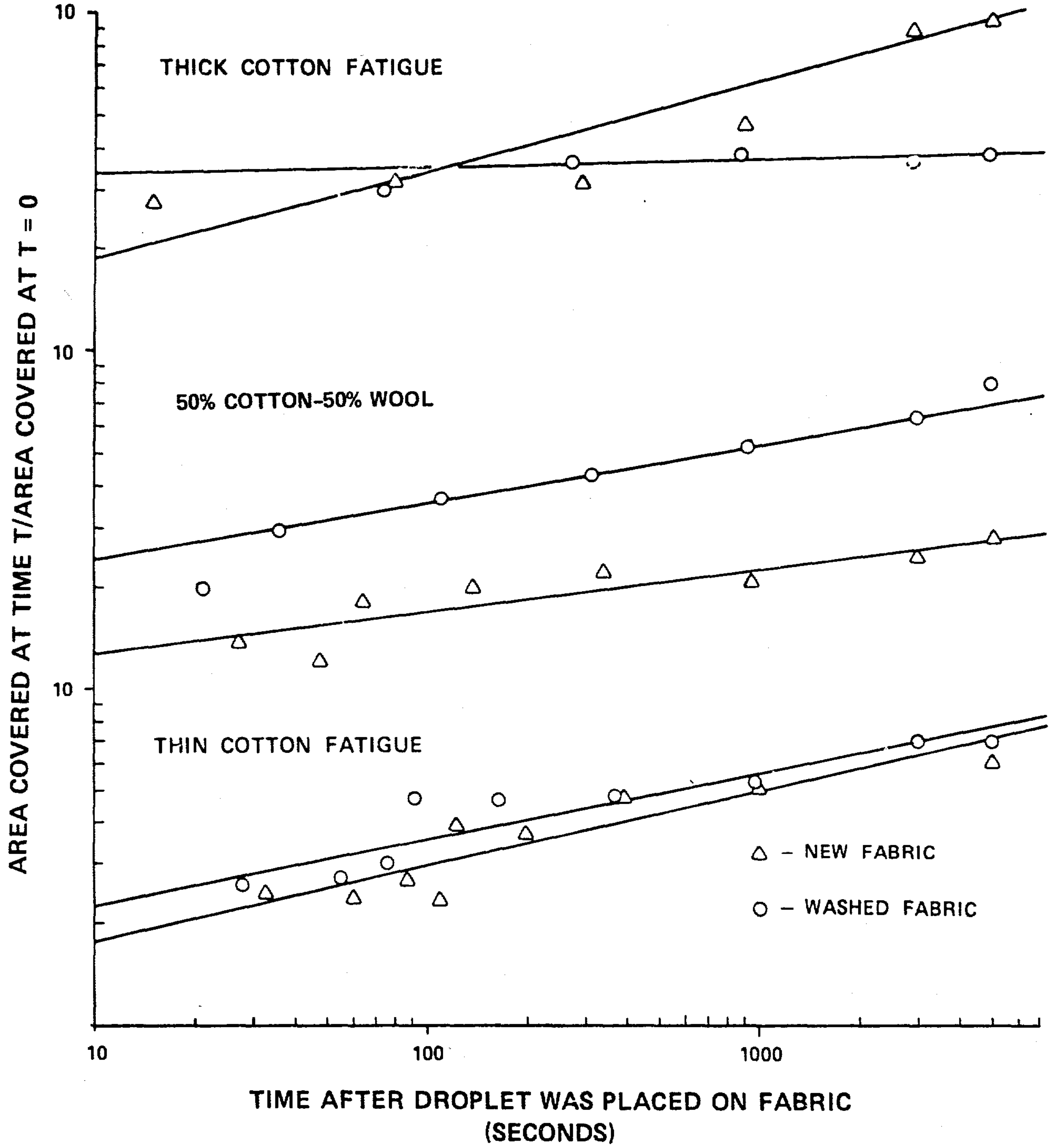

Figure 2. Spread of Neat Bis (4.4-mm Drops) on Fabrics

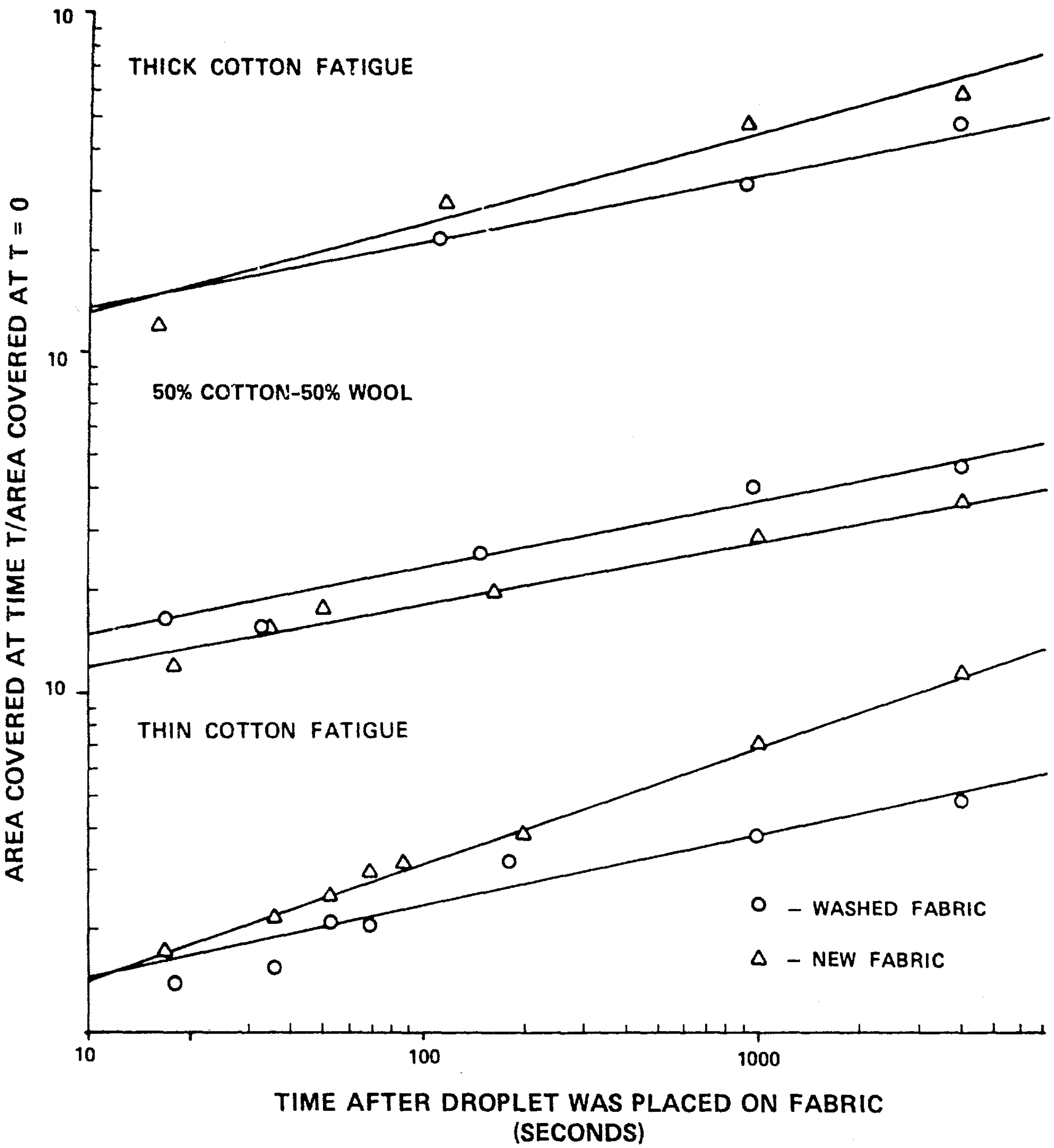

Figure 3. Spread of Thickened Bis (4.0-mm Drops) on Fabrics

These figures are each composed of three sets of graphs. The top part of the graph shows the curves obtained for the thick cotton fabrics, the middle part of the graph shows the curves for the 50% cotton-50% wool material, and the lower part of the graph shows the curves for the thin cotton fabrics. The ordinates for each part of the graph covers the range of 1 to 10. The linearity of the data plots can be seen clearly in most of the curves. There is some scatter in the cases of the thin and thick cotton fatigues, including points representing an area ratio of less than 1. The projected images of the droplets were somewhat irregular in shape and, at times, the edges of the images of the blue-colored spots were not sharply defined against the green color of these fabrics. As a result, the measured area covered may be in error by as much as an estimated 10%. The 50% cotton-50% wool fabric, being almost white, showed the edge of the spot more clearly and there is less scatter in the data for that fabric.

The general equation for a straight-line plot on log-log graph paper can be written:

$$\log (A) = k_1 \log (B) + k_2 \qquad (2)$$

where k_1 and k_2 are constants. In view of the apparent fit shown by the data here to this equation, the constant k_1 in the general equation was computed for these materials using a linear regression procedure. This constant gives the slope of the regression (i.e., least squares) line and is given for the eighteen different fabric-droplet combinations in table 2. As can be seen, the values of this constant vary from 0.04 to 0.34, but the majority of the values are approximately 0.20. The mean for the 18 values is 0.19 and the standard deviation is ± 0.07.

Table 2. Spreading Rate Constant

Fabric	Droplet		
	3.3-mm Neat bis	4.4-mm Neat bis	Thickened bis
New thin cotton fatigue	0.14	0.22	0.34
Washed thin cotton fatigue	0.14	0.18	0.23
New thick cotton fatigue	0.06	0.23	0.18
Washed thick cotton fatigue	0.20	0.04	0.21
New 50% cotton-50% wool	0.19	0.13	0.28
Washed 50% cotton-50% wool	0.18	0.22	0.20

Although the experimental results here do not prove that the value of the constant should be the same for all fabrics, the closeness of the values for most of these fabrics suggests that the constant is most likely the same. This implies that the rate at which this particular liquid spreads in these fabrics is the same without regard to the type of fabric and to any of the physical properties of the fabric.

The value of the spreading rate constant gives a measure of the type of spreading that is occurring. A value of 0 would indicate that there was no spreading occurring at all and that the area wetted at time zero remained constant. If the value of the constant was negative, it would show that the area was decreasing. This type of spreading could occur when the liquid evaporates from the fabric at a rate faster than the rate at which it spreads and the wetted area decreases. Values of the constant greater than zero, as found here, indicate increasing area with time. This constant thus represents factors relating to the volatility of the liquid and to the forces that interact between the liquid and the fabric to cause the liquid to move through the fabric.

In addition to the significance of the spreading rate constant, the results of these experiments do establish that the area covered by the liquid in the fabric is dependent on the logarithm of the elapsed time. The equation is of the form $A = CA_0T^k$ and can be written as

$$\log (A/A_0) = k' \log (T) + C' \qquad (3)$$

In equation 1 it was shown that the penetration of vapor through the fabric was also a function of the logarithm of time. Accordingly, the rate at which the vapor is transported to the second layer has been shown to be proportional to the area wetted by the liquid.

The mechanism controlling the spread of liquid through fabric is plainly a complex one. It is probable that capillary flow and diffusion-type mechanisms are significant. It is also quite likely that comparisons can be made to a chromatographic process in which there is no replenishment of the flowing medium. To identify this primary mechanism was beyond the scope of this study.

The probable dependence of the spread on a chromatographic process may be reflected in the data. As discussed above, the observed area measured was primarily that colored by the methylene blue dye. It was assumed that the dye is carried along at the same rate with the bis as that compound migrates through the fabric. There was no apparent wetting of the fabric beyond the visible edge of the blue dye, and undyed wetted fabric can be detected by eye. As such, it is highly unlikely that the error caused by differing migration rates for the bis and the dye is significant in this study.

The procedure used in these experiments could easily be modified to automate the measurement of the spreading rate by employing an image analyzing system. With the improved precision and speed attainable in measuring the areas by this method, one could predict the relative quantity of vapor that would be transported to the next layer from a liquid droplet placed on the surface of the fabric. This information could be used in determining the protection afforded by different fabrics that were not impregnated with absorbers or decontaminants.

The results of the material transport study conducted earlier,* when combined with the results of this current study, show that the rate of transport of bis vapor to the next layer was proportional to the wetted area, A, raised to a power greater than 1.

$$P \alpha A^n \text{ where } n > 1 \tag{4}$$

The desorption of vapor from a surface is usually described using an equation in the form of the Langmuir adsorption isotherm. There the rate of desorption is directly proportional to the surface area that is covered with the gas molecules. In our study, the area measured was the plane surface area of the fabric. However, the surface area available for vapor desorption in these fabrics is much greater than the plane area. As a result, the measured desorption should be proportional to more than the plane area, which is what was found in this study.

IV. CONCLUSION.

The rate at which a droplet of liquid (bis) wets standard Army fabrics has been measured. The log of the ratio of the area wetted at time T to the area wetted at the time the droplet first contacts the fabric is proportional to the log of T. By comparison with data collected in an earlier study, it is shown that the rate at which vapor from the droplet is transported from a fabric to a second underlying layer is proportional to the area wetted by the liquid.

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